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(54) PROCEDE ET DISPOSIITF POUR PREPARER DES EMULSIONS A BASE DE SILICONE
(54) DEVICE AND METHOD FOR PRODUCING SILICONE EMULSIONS

(57)
The invention relates to a device for producing a silicone and/or silane emulsion consisting of an active component containing silicone and/or silane, and an aqueous phase. Said device comprises a first mixing station for the emulsion components which are delivered by pumps (P1, P2, P3) from reservoirs (VA, VB, VC), and is characterised in that said first mixing station has a mixing device (M1) wherein nozzles (2, 4) mix a jet of the active agent (1) with the aqueous phase (3) to produce a preliminary emulsion. The invention also relates to a method for producing fine-particle, stable silicone emulsions, especially for producing oil-in-water emulsions containing as little emulsifier as possible, and to emulsions produced according to said method.

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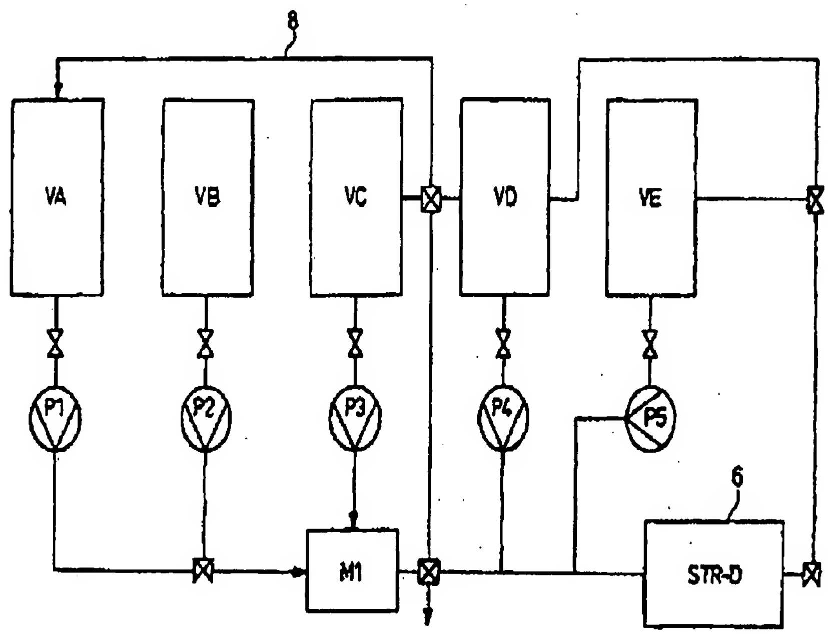
(54) **PROCEDE ET DISPOSIITF POUR PREPARER DES EMULSIONS A BASE DE SILICONE**

(54) **DEVICE AND METHOD FOR PRODUCING SILICONE EMULSIONS**



(57) L'invention concerne un dispositif permettant de préparer une émulsion à base de silicone et/ou de silane, comprenant un principe actif contenant du silicone et/ou du silane et une phase aqueuse. Il est prévu un poste de mélange destiné aux constituants de l'émulsion acheminés depuis des réservoirs (VA, VB, VC) par l'intermédiaire de pompes (P1, P2, P3). Ce dispositif se caractérise en ce que le premier poste de mélange présente un dispositif de mélange (M1) dans lequel des buses (2, 4) mélangent un principe actif en jet (1) avec la phase aqueuse (3) pour former une pré-émulsion. L'invention concerne en outre un procédé de préparation

(57) The invention relates to a device for producing a silicone and/or silane emulsion consisting of an active component containing silicone and/or silane, and an aqueous phase. Said device comprises a first mixing station for the emulsion components which are delivered by pumps (P1, P2, P3) from reservoirs (VA, VB, VC), and is characterised in that said first mixing station has a mixing device (M1) wherein nozzles (2, 4) mix a jet of the active agent (1) with the aqueous phase (3) to produce a preliminary emulsion. The invention also relates to a method for producing fine-particle, stable silicone emulsions, especially for producing oil-in-water

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d'émulsions à base de silicone, stables et à fines particules, s'utilisant notamment pour préparer des émulsions huile dans l'eau avec le moins d'émulsifiant possible, ainsi que des émulsions pouvant être obtenues d'après ce procédé.

emulsions containing as little emulsifier as possible, and to emulsions produced according to said method.

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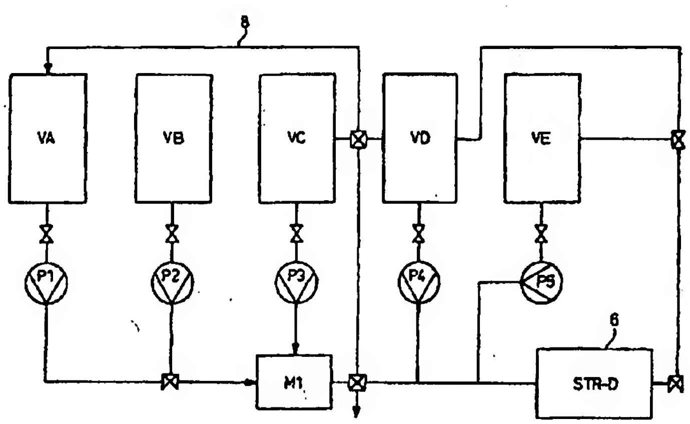
(54) Bezeichnung: VORRICHTUNG UND VERFAHREN ZUR HERSTELLUNG VON SILICONEMULSIONEN



(57) Abstract

The invention relates to a device for producing a silicone and/or silane emulsion consisting of an active component containing silicone and/or silane, and an aqueous phase. Said device comprises a first mixing station for the emulsion components which are delivered by pumps (P1, P2, P3) from reservoirs (VA, VB, VC), and is characterised in that said first mixing station has a mixing device (M1) wherein nozzles (2, 4) mix a jet of the active agent (1) with the aqueous phase (3) to produce a preliminary emulsion. The invention also relates to a method for producing fine-particle, stable silicone emulsions, especially for producing oil-in-water emulsions containing as little emulsifier as possible, and to emulsions produced according to said method.

A process and a device for the preparation of silicone emulsions

The invention relates to a device and to a process for the preparation of fine-particle and stable silicone emulsions, particularly for the preparation of oil in water emulsions with the lowest possible emulsifier content.

A number of processes are known for the emulsification of insoluble silicones and silanes in water. Generally speaking, prior to the actual homogenisation, either small quantities of water are stirred slowly into the silicone in which the emulsifier is finely dispersed, so that a water in oil emulsion is obtained which is inverted by dilution afterwards with water before it is homogenised to a fine-particle emulsion in a special plant, under the action of shear forces, or the silicone is introduced slowly, with stirring, into an aqueous emulsifier mixture before the resulting coarse-particle emulsion undergoes actual homogenisation.

The mixture initially stirred together may already be a sufficiently stable emulsion, depending on the nature of the process and the active substance, the emulsifier concentration, the stirring energy introduced and, above all, the time invested. As a rule, these emulsions, which are known as pre-emulsions, are coarse-particle, however, and must be passed immediately to the actual homogenisation due to lack of stability. Homogenising devices and processes are described in Ullmann's Encyclopedia of Industrial Chemistry Vol A9 Edition 1987, page 309 to 310. The preparation of the pre-emulsion takes place in stirring units and is the rate determining step, depending on the type of downstream homogenising machine.

Further processes for the preparation of silicone emulsions are known from EP-A-043 091 and EP-A 0 579 458. In the process of EP-A-043 091, the entire amount of silicone is fed to a little water with all the emulsifier, so that a high-viscosity paste or a gel is obtained which is then converted to the final emulsion by dilution.

The preparation of the pre-emulsion according to the conventional processes by the addition of the siloxane or silane to the excess water/emulsifier phase becomes problematic, particularly if silicon compounds are used, which may be composed of both monomeric, linear and resin-like structures optionally diluted with low molecular weight siloxanes or organic compounds, if these structures are capable, in principle, of reacting with the aqueous phase. These include, for example, alkylalkoxysilanes, resins bearing alkoxy groups, and optionally mixtures of the two.

A further problem lies in the fact that the preparation of the pre-emulsion according to the known processes is particularly time-consuming. The feed of the siloxane component into the aqueous phase takes place in a controlled manner with stirring, i.e. in such a manner that optimum mixing is obtained. This does not permit a rapid addition.

The first molecules of the active substance meet a huge excess of water which approaches the desired concentrations only during the course of time, and provides a coarse-particle, unstable pre-emulsion which must be fed to the homogeniser as quickly as possible.

During this addition, water-sensitive components, if used, are protected only inadequately from the attack of the aqueous phase, even if the latter is buffered, so that the reaction of the corresponding components amongst themselves may occur. This may cause the subsequent homogenisation to be more difficult due to a condensation process, followed by a build up of viscosity in the resulting coarse emulsion particles, or may cause the pre-emulsion to become so unstable that it can no longer be fed to the homogeniser. Although this shortcoming may be counteracted by a substantial increase in the emulsifier (in the region of 5%), this leads to unwanted results in many applications and to environmental pollution.

Moreover, e.g. in the case of alkylalkoxysilanes, hydrolysis and condensation reactions during emulsification usually lead to the ineffectiveness of the resulting emulsion during use, and thus to its unsuitability.

If the pre-emulsion is prepared by way of a paste or a gel, which are diluted afterwards in a special process, emulsions with low average particle sizes can be prepared in cases where no importance is attached to emulsifier contents, although no details are given about the particle size distribution thereof.

As there are a number of silicone active substances which provide pastes only to an unsatisfactory degree, at least with the emulsifier quantities required, these processes are restricted in terms of their range of application. Moreover, a number of emulsions such as, e.g., defoamer emulsions or emulsions with a low emulsifier content (<5%) and at the same time a low active substance content (≤ 20%) cannot be prepared satisfactorily according to this process. So emulsions with very large particles in the region of 3-60 µm are obtained in a very time-consuming manner in the process according to EP 0 579 458 (see examples therein).

The object of the present invention was, therefore, to provide a rapid and thus economic process which does not have the disadvantages described and permits the preparation of fine-particle emulsions with narrow particle size distributions and low emulsifier contents and low to high concentrations of active substance, and to provide a device suitable for said process. Water-sensitive active substances were to lead to stable - even for more than a year - and above all effective emulsions.

A particular aim, i.a. in order to achieve high reproducibility, was to bring the quantities of emulsion required for a certain surface coating of the active substance particles into contact ab initio with the active substance and to match the mechanical energy hereto. This presupposed a process with emulsifying devices that

can be described precisely mathematically. Devices that are greatly affected by the residence time are unsuitable (e.g. stirring units, etc.).

Finally, the energy to be introduced was to cover a broad range - a situation which could be achieved hitherto only by means of several devices with different structures. It is thus possible to prepare, in the same plant, emulsions which have to be protected from a high energy input, - e.g. defoamer emulsions - as well as emulsions which require a multiple of the energy supplied by conventional homogenisers.

The object in question could be achieved by means of a device composed of storage vessels, pumps and nozzles, hereinafter referred to as a mixing station. It proved to be particularly advantageous if this mixing station was followed by a jet disperser of the kind described for the preparation of pharmaceutical or cosmetic dispersions (Bayer AG / EP 0 101 007).

The invention relates, therefore, to a device for the preparation of a silicone, silane or silicone/silane emulsion composed of a silicone-containing and/or silane-containing active substance component and an aqueous phase (component), with a first mixing station for the emulsion components fed via pumps P1, P2, P3 from storage tanks (VA, VB, VC), the first mixing station having a mixing apparatus M1 in which nozzles 2,4 mix a jet of active substance with the aqueous phase 3 to a pre-emulsion (see Fig. 1 and 2).

In a preferred embodiment of the device according to the invention, the first mixing station is connected to a high-pressure homogeniser, the high-pressure homogeniser containing the pre-emulsion leaving the mixing station.

The invention also relates to a process for the preparation of fine-particle aqueous silicone and/or silane emulsions with a narrow particle size distribution, comprising

- the preparation of a pre-emulsion by injecting the silicone and/or silane component into an aqueous phase containing emulsifier in a mixing station and

- homogenisation in a high-pressure homogeniser, and the emulsions of silicone compounds and/or silanes which may be obtained according to this process.

In particular, the invention relates to a process for the preparation of fine-particle aqueous silicone and/or silane emulsions with a U_{90} value of less than 1.2 (i.e. with a narrow particle size distribution), comprising

- the preparation of a pre-emulsion by injecting the silicone and/or silane component into an aqueous phase containing emulsifier in a mixing station, whereby a pressure difference of a maximum of 10 bar is maintained between both streams, depending on the nozzle dimensions, with an absolute pressure drop of less than 100 bar, and

- homogenisation of the pre-emulsion.

The present invention is explained in more detail by the attached Figures and Examples.

Fig. 1 shows a mixing station;

Fig. 2 is a schematic representation of the device according to the invention with a high-pressure homogeniser;

Fig. 3 shows the nozzle arrangement of a jet disperser;

Fig. 4 shows a high-pressure homogeniser;

Fig. 5, 6, 7 and 8 show the differential and integral particle size distribution of Example 10, 9, 18 and 19.

In the device according to the invention with a known pressure drop $(\Delta p)^{STR\text{-}D}$, a known emulsifier content and surface requirement, a known nozzle diameter $(D)^{STR\text{-}D}$, a known interfacial surface tension (γ), a known viscosity (η) of the disperse phase and a known number of passes $(n)^{STR\text{-}D}$, the expected average particle size (d) may be calculated from the following formula:

$$d = k \text{ A } (\Delta p)^{-0.6} \text{ A } \eta^{0.495} \text{ A } \gamma^{0.365} \text{ A } D^{0.165} \text{ A } n^{0.36}$$

k = constant (relating to emulsifier content/surface requirement).

The core of the mixing station is a nozzle arrangement in a mixing apparatus M1, the dimensions of which depend on the consistency of the two phases to be combined, their concentration with respect to one another, the pressure drop chosen, and the throughput.

Fig. 1 shows a possible embodiment. For example, the silicone oil 1 is injected into the aqueous phase 3 via the first nozzle 2 and immediately afterwards is mixed intensively and homogenised in the second nozzle 4. The final fine dispersion then takes place in the downstream jet disperser STR-D. The jet disperser STR-D may be immediately downstream or, in a batchwise operation, only after the preparation of the entire pre-emulsion 5.

The nozzle arrangement according to Fig. 1 is preferably fed by means of two pumps P1, P3 with a pressure difference of 2-3 bar in such a way that - where the coating speed of the emulsifier permits - the aqueous emulsifier solution and the silicone are

fed together in the final emulsion concentration and homogenised directly by means of the jet disperser STR-D in one or a maximum of three passes.

The number of passes usually depends on the nature and content of the emulsifier. Emulsifier contents in the region of 3% make only one pass necessary - exceptions apart.

If emulsifiers are present that coat the surfaces of the resulting particles of certain silicone active substances only relatively slowly, the process may be modified in such a way that operations are carried out with any deficient amount of water containing the entire quantity of emulsifier. The more concentrated emulsion obtained in this case may be returned to the aqueous emulsifier solution and fed with the latter back to the nozzle and to the inflowing active substance, so that a circuit is obtained. Whether the circuit remains intact for a few minutes after the substances have been combined depends on the concentration and nature of the emulsifier and on the silicone to be emulsified. The remainder of the water to which further additives e.g. thickeners or preservatives are optionally added may be added to the circuit by way of a further nozzle and pump before this pre-emulsion is fed to the jet disperser STR-D.

Fig. 4 shows the jet disperser STR-D which is used as high-pressure homogeniser 6. The jet disperser STR-D is composed more specifically of a pump 14, optionally a pulsation damper 16 and a nozzle arrangement 18, which is shown in detail in Fig. 3. The two-stage nozzle arrangement 18 has a first nozzle 10 and a downstream second nozzle 12, with the aid of which the pre-emulsion 5 is homogenised. Each nozzle 10, 12 is composed of an insert part 11 in a tube 9, each insert part 11 having a cylindrical section 13 protruding against the direction of flow of pre-emulsion 5, with two opposite capillary holes 15. The cylindrical section 13 forms an annular space 17 in the tube 9, pre-emulsion 5 flowing through the tube 9 into the annular space 17 and from there through capillary holes 15 into an intermediate chamber 20.

As the capillary holes 15 are opposite each other, the emerging jets of emulsion collide with one another inside the cylindrical section 13. As a result, a particularly good dispersion is achieved. The emulsion flows out of intermediate chamber 20 into a second annular space 22 of the second nozzle 12 where it again passes through the capillary holes 24 of the second nozzle 12. The homogenised emulsion 25 leaves the jet disperser STR-D through the outlet 26.

The present invention also allows the ratio of the water - containing all the emulsifier- to active substance to be chosen in such a way that gels and pastes are also obtained. The proviso is that the pumps chosen are of the positive conveying type and control the consistency of the pastes.

An advantage of the present invention is that it is able to operate practically continuously, is not very time-consuming, and has outstanding reproducibility. It provides stable emulsions of which the average particle sizes have values of <1 µm, with emulsifier contents in the region of 0.5 - 3%. The particle size distribution which is important for the stability and for many applications lies in a narrower range than is the case with the conventional processes.

There are also a few cases, however, where rather unstable emulsions are produced in which both the particle size and the particle size distribution do not play an important part, with the result that, for cost or other reasons, a subsequent homogenisation is dispensed with after the passage through the mixing station. The lack of stability of these emulsions may be offset in such cases by substantially increasing the emulsion viscosity by adding a neutral thickener. In view of the often poor processability of such emulsions, attempts are usually made to avoid this method of production.

The above-mentioned emulsions also include a few emulsions with a high viscosity in which an indispensable high-viscosity active substance - e.g. of an organic nature - is responsible for this.

Naturally, it would be uneconomic in such cases to emulsify such emulsions afterwards additionally in the jet disperser STR-D because - were the present state of the emulsion to be essentially maintained - the jet disperser would not be able make a significant contribution towards improving the physical properties of the emulsion under the process conditions required for this purpose.

In this case it is advisable to homogenise the pre-emulsion leaving the mixing station in a second mixing station with a higher pressure, e.g. up to 100 bar.

This method is also recommended if readily emulsifiable Si compounds are to be emulsified with emulsifiers that have a sufficient particle surface coating speed. In this case, it is possible to dispense with thickeners.

In order to minimise the apparatus required, however, it is preferable to transfer the pre-emulsion to a storage tank upstream of the first mixing station and to bring it from there via the same mixing station under different pressure conditions to the desired emulsion state.

The invention thus also relates to a process for the preparation of fine- to coarse-particle aqueous silicone and/or silane emulsions in the region of about 0.4 to 5.0 µm with a U_{90} value greater than 1.1 (i.e. broader particle size distribution) which require only low shear forces for emulsification and are stabilised by thickeners, comprising

- the preparation of a pre-emulsion by injecting the silicone and/or silane component into an aqueous phase containing emulsifier in a mixing station, a

pressure difference, dependent on the nozzle dimensions, of a maximum of 10 bar being maintained between the two streams with an absolute pressure drop of less than 80 bar,

- homogenisation of the pre-emulsion in a downstream mixing station or at a later stage in the same mixing station with an absolute pressure drop of up to 100 bar.

An embodiment is obtained from Fig. 2, in which

VA: active substance container
VB: residual water container (+ additives)
VC: buffer vessel / intermediate container
VE: storage tank / intermediate container
VD: buffer vessel
P1, P2: pumps (optionally forced conveying pumps)
P3, P4, P5: pumps
M1: mixing nozzle for active substance/water
STR-D: jet disperser.

In the active substance circuit VA→P1→M1→VA the aqueous phase is injected at low pressure via VC→P3→M1 and after the addition is completed the circuit VA→P1→M1→VA is switched to higher pressure, M1 acting as a downstream homogeniser. The emulsion may be removed behind M1.

The proviso is, of course, that the emulsifiers have a sufficiently high particle coating speed, a property which also depends on the ability of the active substance to adsorb these emulsifiers.

Examples of the silicone and silane component are

- silicone compounds with the usual composition:

$(CH_3)_3SiO[(CH_3)_2SiO]_{50-500}Si(CH_3)_3$

$HO(CH_3)_2SiO[(CH_3)_2SiO]_{500}Si(CH_3)_2OH$

$(CH_3)_3SiO[(CH_3)(H)SiO]_{50}Si(CH_3)_3$

$(CH_3)_3Si(O)_{1.1}(OCH_3)_{0.8}$;

- organoalkoxysilanes, hydrolysis products thereof, e.g.:

$CH_3(CH_2)_7Si(OEt)_3$

$CH_3(CH_2)_3Si(OEt)_3$

$CH_3(CH_2)_{11-13}(CH_3)Si(OMe)_2$

$CH_3(CH_2)_7Si(OEt)_2O(OEt)_2Si(CH_2)_7CH_3$

$CH_3(CH_2)_3Si(OEt)_2[O(EtO)Si(CH_2)_3CH_3]_{0-5}OSi(OEt)_2(CH_2)_3CH_3$;

- linear polyorganosiloxanes with and/or without silicon-functional bound groups such as hydrogen, alkoxy, polyether and hydroxy groups, with and/or without organofunctionally attached groups such as polyethers, amines or halogens or pseudohalogens, e.g.:

$(CH_3)_3SiO[(CH_3)_2SiO]_{50-500}Si(CH_3)_3$

$HO(CH_3)_2SiO[(CH_3)_2SiO]_{500}Si(CH_3)_2OH$

$(CH_3)_3SiO[(CH_3)(H)SiO]_{50}Si(CH_3)_3$

$(CH_3)_3SiO[(CH_3)CH_2{=}CHSiO]_3\,[(CH_3)_2SiO]_{50-500}Si(CH_3)_3$

$(CH_3)_3SiO[CH_3(OCH_2CH_2)_8O(CH_2)_3(CH_3)SiO]_3[(CH_3)_2SiO]_{600}Si(CH_3)_3$

- branched polyorganosiloxanes with and/or without attached silicon-functional groups such as hydrogen, alkoxy, polyether and hydroxy groups with and/or without organofunctionally attached groups such as polyethers, amines or halogens or pseudohalogens, e.g.:

$CH_3Si\{[(CH_3)_2SiO]_{50}OSi(CH_3)_3\}_3$

$CH_3Si\{[(CH_3)_2SiO]_{80}OSi(CH_3)_2CH_2{=}CH_3\}_3$

$CH_3Si\{[(CH_3)_2SiO]_{90}OSi(CH_3)_2(CH_2)_3(OCH_2CH_2)_8OCH_3\}_3$
$H_2N(CH_2)_3Si\{[(CH_3)_2SiO]_{18}OSi(CH_3)\}_3$;

- silicone resins with aryl-, alkyl- organofunctionally modified alkyl groups, alkoxyfunctional resins with or without diluents, e.g.:

$(CH_3)_{1.16}Si_1O_{1.42}$
$(CH_3)_{0.8}(C_{12}H_{25})_{0.2}Si(O)_1(OCH_3)_1$
$(SiO_2)_{10}[(CH_3)_3SiO_{1/2}]_{0.8}$
$SiO_2[(CH_3)CH_2{=}CHSiO]_{0.3}[O_{1/2}Si(CH_3)_3]_{1.2}$

- mixtures of the above components or with insoluble additives of a mineral or organic nature.

The term emulsifiers means ionic and nonionic emulsifiers of the kind customarily used in silicone emulsification, and mixtures thereof.

Suitable ionic emulsifiers are, depending on the active substance, e.g.:

- alkylsulfonates with 8 to 18 C atoms with or without ethylene- or propylene oxide units;

- sulfate esters such as, e.g., $CH_3(CH_2)_6CH_2O(C_2H_4O)_{6\text{-}19}SO_3H$;

- alkylarylsulfonates, such as, e.g., dodecylbenzene sulfonate;

- quaternary ammonium compounds such as, e.g., dodecyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxides and salts thereof.

Nonionic emulsifiers of which the HLB value is from 10 to 16 are, however, preferred. If mixtures within this range are present they may be composed of combinations of emulsifiers with an HLB value between 2.7 and 18.7.

Suitable nonionic emulsifiers are adducts of ethylene oxide and fatty alcohols, alkyl phenols, triglycerides or sugar; polyethylene oxide sorbitan laurates, palmitates and stearates; adducts of ethylene oxide and alkylamines; and polyvinylalcohols (such as Mowiol), particularly ethoxy adducts with tridecyl alcohol, ethoxy adducts with sorbitan monooleates (Tween® products from ICI), sorbitan monooleates and mixtures thereof.

The average particle diameter - in the text also called the particle size - is calculated from the volumetric mean which is obtained from the total volume of all the particles of the emulsion divided by the number of particles.

The numerical value of the breadth of the particle size distribution was calculated in such a way that, out of the given quantity of particles, the particles with the smallest diameters up to a quantity of 10 wt.% of the particle quantity (d10) and the particles with the largest diameters up to a quantity of 10 wt.% of the particle quantity (d90) are not taken into account, and the difference in the diameters of the remaining largest particle and of the remaining smallest particle is divided by the diameter of that particle (d50) that is greater than 50 wt.% of all the particles and smaller than 50 wt. % of all the particles. This numerical value is hereinafter called U_{90}:

$$U_{90} = \frac{d90 - d10}{d50}$$

(see Fig. 5, 6, 7 and 8).

The average particle sizes were measured by Fraunhofer diffraction, ultracentrifugation or by photometry with the aid of Mie theory. The distribution curves were measured by means of the ultracentrifuge.

The apparatus shown in the appendix in a schematic flow diagram (Fig. 2) allows process adjustments tailored in a flexible manner to the active substance, the emulsifier and the concentrations thereof.

For example, in the favourable case when readily emulsifiable products are present, the emulsifier is "rapid" and present in a favourable concentration, the active substance (from VA) may be fed together with the water/emulsifier mixture (from VC) in the desired ratio to M1, and the resulting pre-emulsion fed directly or via a buffer vessel (VD) to the jet disperser STR-D, homogenised in one pass and then fed to the filling station.

This procedure requires reliable control or synchronisation of the pumps. If this is to be dispensed with and if an exact ratio of emulsifier/active substance is not absolutely necessary during the combined feed to M1, it is possible, in order nevertheless to guarantee the necessary active substance concentration in the emulsion, to feed the active substance to a calculated deficient amount of water/emulsifier mixture via M1, to return the resulting pre-emulsion constantly to the water/emulsifier mixture (after VC) and to feed it together again with the active substance in the circuit via M1. If the entire active substance is consumed, the pre-emulsion is brought to the final concentration via the nozzle M1 by adding the remaining water (from VB) by means of a circuit similar to the one just described (M1→VC→M1) and homogenised as above.

In the case of active substances that are difficult to emulsify, "slow" emulsifiers or very low emulsifier concentrations, pre-emulsification can be carried out a couple of

times via VC and MI in the circuit before feeding to STR-D, prior to operating as above.

If a paste or a gel is considered important and if the active substance is suitable for this, it may be fed together with any deficient amount of water (from VC) - but all the emulsifier - into M1, and resulting emulsion returned to VC, as above, and atomised with its contents repeatedly via M1 with the active substance. A high-viscosity pre-emulsion is thereby obtained, which may have a paste or gel consistency depending on the conditions chosen.

Said emulsions may - depending on the intended application - be filled as such or processed further as described below.

Before being homogenised above in STR-D, it is passed via M1, where the remaining water (from VB), optionally with thickener and other conventional additives, is injected so that the calculated composition is obtained.

If more than one pass through STR-D is required, another cycle via VE→STR-D may be carried out before the emulsion is filled.

If several discrete passes are desired, however, it is possible to carry out emulsification from the buffer vessel VD via STR-D in one pass after VE, after completion from there in a second pass via STR-D again to VD, etc.

In the examples that follow, all the data relate to weight, unless otherwise specified.

The following abbreviations are used:

Me: $-CH_3$

Et: $-C_2H_5$

Octeo: $C_8H_{17}Si(OEt)_3$

V: pre-emulsion

Only the time required for the preparation of the pre-emulsion is given in the Tables, since the preparations for the water/emulsifier mixtures are practically the same in the examples according to the invention and those not according to the invention. The actual homogenisation stage was likewise not included in the consideration of time, since it is largely dependent on the capacity of the emulsifying devices in the comparison.

In the Tables, the examples according to the invention are printed in bold and the comparative examples in italics.

Examples

A. Resin emulsions

Example 1 (Comparative example)

238.7 g of distilled water were heated to 60°C in a 2 l vessel and 55 g of a melted mixture - corresponding to 2.50% based on the total batch - of a POE-stearyl alcohol and a POE-cetyl alcohol with a total HLB value of 15.5 were added with stirring.

After cooling to 40°C, 1447.6 g of an Isopar® G solution with 80% resin with an average composition $(CH_3)_{1.16}\ Si_1\ O_{1.42}$ and a viscosity of 1620 mPa.s were added within one hour at a rate of stirring of 250 - 400 rpm. Stirring was continued for 10 min at a rate of stirring of ~ 400 rpm. 458.7 g of an aqueous solution of 1.76 g of carboxymethylcellulose (Walocel CRT 5000 GA) were added with stirring within 25 min. Stirring was continued for 40 min.

The pre-emulsion was homogenised in six passes in a conventional high-pressure homogeniser of the Gaulin type with a pressure drop of ΔP = 250 bar. The results are given in Table 1.

Example 2 (Comparative example)

Example 1 was repeated with a total emulsifier content of 3.00%. The results are given in Table 1.

Example 3

The same batch as in Example 1 - but with 2.2% emulsifier mixture - was increased by a factor of 2.7273. 645.0 g of distilled water were heated to 50°C in VC (see

attachment Fig. 2) and 133 g of a melted mixture - corresponding to 2.20% based on the total batch - of a POE-stearyl alcohol and an PEO-cetyl alcohol with a total HLB value of 15.5 were added with stirring, and forced by means of P3 at 3 bar through M1 (nozzle diameters 2.1/1.0 mm) to VC and circulated for 30 s by means of P3 through M1 to VC. 3948 g of the same resin as in Example 1 were injected into this circuit within 17 min from VA by means of P1 at 5 bar into M1. The circuit was then maintained for 10 min, then an aqueous solution of 4.8 g of carboxymethylcellulose (Walocel CRT 5000 GA) in 1264.2 g of water were injected into the circuit within 9 min from VB via M1. After the addition was completed, the circuit was maintained for another 40 min before the pre-emulsion was homogenised in three passes in the jet disperser STR-D (nozzle diameter: 0.2828 mm) with a pressure drop of $\Delta P = 250$ bar. The results are given in Table 1.

Example 4

Example 3 was repeated with a total emulsifier content of 2.5%. The results are given in Table 1.

Example 5

Example 3 was repeated with a total emulsifier content of 2.8%. The results are given in Table 1.

Example 6

Example 3 was repeated with a total emulsifier content of 3.0%. The results are given in Table 1.

Table 1

Pass no.						Particle size Ø [µm]						Stability [months]					
←Example→						←Example→						←Example→					
1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
V	V	V	V	V	V	>5.000	>5.000	>5000	>5000	5000	>5000	0	0	0	0	0	0
1	1	1	1	1	1	4.954	4.760	2.915	2.550	2.453	2.106	/	/	/	/	/	/
2	2	2	2	2	2	4.687	4.487	2.143	0.653	0.660	0.634	0.5	0.5	>6	>6	>6	>6
3	3	3	3	3	3	4.423	4.390	1.617	0.642	0.593	0.589	0.5	0.5	>6	>6	>6	>6
4	4					4.343	4.202					0.5	0.5				
5	5					4.216	4.068					0.5	0.5				
6	6					4.094	3.989					0.5	0.5				

B. Resin/silane (water-sensitive) emulsions

Example 7 (Comparative example)

In a 4 l agitated vessel, 816.22 g of water and 2.18 g of diethanolamine were added to 22 g of emulsifier mixture - corresponding to 1 wt.%, based on the total batch - of an ethoxylated sorbitan monolaurate and an ethoxylated oleyl alcohol with a total HLB value of 15.3 and stirred for 2 hours at 80°C, a clear solution being obtained. 1359.6 g of a mixture of 49.2% octyl triethoxysilane and 50.8% of a resin with the composition $(CH_3)_{0.8}(C_{12}H_{25})_{0.2}$ $Si(O)_1$ $(OCH_3)_1$ were added to the cooled solution within 65 min at a rate of stirring of 700 rpm. After the addition was completed, stirring was continued for 30 min at 550 rpm. A sample was taken after 30 min for particle size determination. The pre-emulsion was homogenised in 2 passes in a conventional homogeniser of the Gaulin type with a pressure drop of $\Delta P = 250$ bar. The results are given in Table 2.

Example 8

The batch from Example 7 was doubled. 1632.44 g of water and 4.36 g of diethanolamine were added to 44 g of emulsifier mixture - corresponding to 1 wt.%, based on the total batch - of an ethoxylated sorbitan monolaurate and an ethoxylated oleyl alcohol with a total HLB value of 15.3 in VC (see Fig. 2) and stirred for 2 hours at 80°C, a clear solution being obtained. After cooling, the solution was pumped for one minute at 3 bar in the circuit VC→P3→M1→VC. 2719.2 g of a mixture of 49.2% octyltriethoxysilane and 50.8% of a resin with the composition $(CH_3)_{0.8}(C_{12}H_{25})_{0.2}Si(O)_1(OCH_3)_1$ were injected into this circuit at 5 bar from VA by means of P1 and through M1 (nozzle diameters: 2.1/1.0 mm) within 3.5 min. After the addition was completed, the above circuit was maintained for another 15 min at 3 bar. A sample was taken after 5 and 15 min for a particle size determination. The

pre-emulsion was homogenised in 2 passes with a pressure drop of ΔP = 100 bar. The results are given in Table 2.

Example 9 (Comparative example)

In a 4 l agitated vessel, 163.2 g of water and 2.18 g of diethanolamine were added to 22 g of emulsifier mixture - corresponding to 1 wt.%, based on the total batch - of an ethoxylated sorbitan monolaurate and an ethoxylated oleyl alcohol with a total HLB value of 15.3 and stirred for 2 hours at 80°C, a clear solution being obtained. 1359.6 g of a mixture of 49.2% octyltriethoxysilane and 50.8% of a resin with the composition $(CH_3)_{0.8}(C_{12}H_{25})_{0.2}\ Si(O)_1\ (OCH_3)_1$ were added to the cooled solution within 65 min at a rate of stirring of 700 rpm. After the addition was completed, stirring was continued for 15 min at 550 rpm, a high-viscosity paste being obtained. 653.0 g of water were added at the above-mentioned rate of stirring within 30 min and stirring was continued until the particle size had fallen below 5 µm (45 min). The pre-emulsion was homogenised in 2 passes in a conventional homogeniser of the Gaulin type with a pressure drop of ΔP = 200 bar. The results are given in Table 2.

Example 10

The batch from Example 9 was tripled. 489.60 g of water and 6.54 g of diethanolamine were added to 66 g of emulsifier mixture - corresponding to 1 wt.%, based on the total batch - of an ethoxylated sorbitan monolaurate and an ethoxylated oleyl alcohol with a total HLB value of 15.3 in VC (see Fig. 2) and stirred for 2 hours at 80°C, a clear solution being obtained. After cooling, the solution was pumped for one minute at 3 bar in the circuit VC→P3→M1→VC. 4078.8 g of a mixture of 49.2% octyltriethoxysilane and 50.8% of a resin with the composition $(CH_3)_{0.8}(C_{12}H_{25})_{0.2}\ Si(O)_1\ (OCH_3)_1$ were injected into this circuit at 5 bar from VA by means of P1 and through M1 (nozzle diameters: 2.1/1.0 mm) within 5 min. After the addition was completed, the above circuit was maintained for another 4 min at 3

bar. 1959 g of water were then injected into the above circuit via M1 from VB within 10 min. After all the water had been added, the pre-emulsion was pre-homogenised in the circuit for another 1 min, a sample was taken for determining the particle size, and homogenisation was carried out in two passes in the jet disperser with a pressure drop of ΔP = 100 bar. The results are given in Table 2.

Table 2

Pass no.				Pressure drop ΔP [bar]				Particle size Ø [µm]				Pre-emulsion Time required [min]				Distribution U_{90}			
Example				Example				Example				Example				Example			
7	**8**	*9*	**10**	*7*	**8**	*9*	**10**	*7*	**8**	*9*	**10**	*7*	**8**	*9*	**10**	*7*	**8**	*9*	**10**
V	**V**	*V*	**V**	*0*	**3/5**	*0*	**3/5**	*>5.000*	**3.773**	*4.241*	**4.371**	*95*	**20***	*110*	**21+**				
I	**I**	*I*	**I**	*250*	**100**	*200*	**100**	*1.766*	**0.647**	*0.763*	**0.632**					*2.03*	**1.21**	*1.75*	**1.21**
2	**2**	*2*	**2**	*250*	**100**	*200*	**100**	*1.707*	**0.609**	*0.548*	**0.583**					*1.32*	**1.02**	*1.21*	**1.10**

* with a double batch

\+ with a triple batch

Example 11

390.83 g of water and 3.17 g of diethanolamine were added to 32 g of emulsifier mixture - corresponding to 0.64 wt.%, based on the total batch - of an ethoxylated sorbitan monolaurate and an ethoxylated oleyl alcohol with a total HLB value of 15.3 in VC (see Fig. 2) and stirred for 2 hours at 80°C, a clear solution being obtained. After cooling, the solution was pumped for one minute at 3 bar in the circuit VC→P3→M1→VC. 1980 g of a mixture of 49.2% octyltriethoxysilane and 50.8% of a resin with the composition $(CH_3)_{0.8}(C_{12}H_{25})_{0.2}Si(O)_1(OCH_3)_1$ were injected into this circuit at 5 bar from VA by means of P1 and through M1 (nozzle diameters: 1.8/0.9 mm) within 3 min. After the addition was completed, the above circuit was maintained for another 2 min at 3 bar. 2594 g of water were then injected into the above circuit via M1 from VB within 13 min. After all the water had been added, the pre-emulsion was pre-homogenised for 4 min in the circuit, a sample was taken for determining the particle size and homogenisation was carried out in 2 passes in the jet disperser with a pressure drop of $\Delta P = 95$ bar. The results are given in Table 3.

Table 3

Pass no.	Pressure drop ΔP [bar]	Particle size Ø [μm]	Pre-emulsion time required [min]	Emulsifier content [%]	Emulsion stability [months]
V	3/5	4.326	25	0.64	-
1	95	0.621			>6
2	95	0.611			>6

C. Silicone oil emulsions

Example 12

1850 g of water were added at 50°C to 150 g of melted emulsifier mixture - corresponding to 3 wt.% based on the total batch - of an ethoxylated triglyceride and an ethoxylated tridecylalcohol with a total HLB value of 13.5 in VC (see Fig. 2) and pumped for 2 min at 3 bar in the circuit VC→P3→M1→VC, cooled, and 3000 g of a diorganopolysiloxane having a viscosity η = 350 mPas were injected into this circuit within 18 min from VA by means of P1 at 5 bar into M1 (nozzle diameters 1.4/0.7 mm). Homogenisation was then carried out in STR-D with a pressure drop of 250 bar. The results are given in Table 4.

Example 13

1550 g of water were added at 45°C to 200 g of melted emulsifier mixture - corresponding to 4 wt.% based on the total batch - of an ethoxylated triglyceride and an ethoxylated tridecylalcohol with a total HLB value of 15.4 in VC (see Fig. 2) and pumped for 2 min at 3 bar in the circuit (nozzle diameters 1.4/0.7 mm), cooled, and 1750 g of a diorganopolysiloxane having a viscosity η = 350 mPas were injected into this circuit within 5.5 min from VA by means of P1 at 5 bar into M1 (nozzle diameters 2.1/1.0 mm). After the addition was completed, pumping was continued in the circuit for another 5 minutes at 3 bar. 1500 g of water from VB were then injected via M1 at 5 bar within 8 minutes. After a further 5 min circuit at 3 bar, homogenisation was carried out in STR-D with a pressure drop of 250 bar. The results are given in Table 4.

Example 14

1240 g of water were added at 50°C to 180 g of melted emulsifier mixture - corresponding to 4.5 wt.% based on the total batch - of an ethoxylated triglyceride and an ethoxylated tridecylalcohol with a total HLB value of 15.4 in VC (see Fig. 2) and pumped for 1 min at 3 bar in the circuit VC→P3→M1→VC, cooled, and 800 g of a diorganopolysiloxane having a viscosity η = 350 mPas were injected into this circuit within 1.5 min from VA by means of P1 at 5 bar into M1 (nozzle diameters 2.1/1.0 mm). After the addition was completed, pumping was continued in the circuit for another 2 minutes at 3 bar. 1780 g of water from VB were then injected via M1 at 5 bar within 8.5 minutes and homogenisation was carried out in the same circuit for 2 min at 3 bar. Homogenisation was then carried out in STR-D with a pressure drop of 200 bar. The results are given in Table 4.

Example 15 (Comparative example)

620 g of water were added at 50°C to 90 g of melted emulsifier mixture - corresponding to 4.5 wt.% based on the total batch - of an ethoxylated triglyceride and an ethoxylated tridecylalcohol with a total HLB value of 15.4 in an agitated vessel and stirred for 3 min, cooled, and 400 g of a diorganopolysiloxane having a viscosity η = 350 mPas were added via a dropping funnel with stirring within 13 min. After the addition was completed, stirring was continued for another 5 minutes at 400 rpm before 890 g of water were added within 27 minutes at 300 rpm (considerable foaming). The pre-emulsion was homogenised in a conventional homogeniser of the Gaulin type in 2 passes with a pressure drop of ΔP = 200 bar. The results are given in Table 4.

Table 4

Pass no.				Particle size ∅ [µm]				Pre-emulsion time required [min]				Active substance concentration [%]				Emulsion stability [months]			
Example				Example				Example								Example			
12[1]	13[2]	14[3]	*15*[4]	12	13	14	*15*	12	13	14	*15*	12	13	14	*15*	12	13	14	*15*
V	V	V	*V*	-	-	-	-	18	23.5	14	*45*	60	35	20	*20*	-	-	-	-
1	1	1	*1*	1.0	0.960	2.743	*3.411*					60	35	20	*20*	>6	>6	6	
2	2	2	*2*	0.9	0.832	0.910	*3.317*					60	35	20	*20*	>6	>6	6	
3	3	3	*3*	0.8	0.787	0.822	*2.534*					60	35	20	*20*	>6	>6	6	*<6*
	4	4	*4*		0.777	0.798	*2.406*										>6	6	*<6*
							2.362												*<6*
							2.254												*<6*

1) 5000 g batch

2) 5000 g batch

3) 4000 g batch

4) 2000 g batch

Example 16

2800 g of water, 4.6 g of 37% hydrochloric acid, 5.25 g of glycine, 51.3 g of glycerol, 200 g of an alkylbenzylammonium bromide, 30 g of an ethoxylated tridecylalcohol with an HLB value of 11.4 and 22.6 g of glycol were charged to VC (see Fig. 2) and pumped in the circuit VC→P3→M1→VC for 30 s at 3 bar. 2056 g of a hydrogen-bearing organopolysiloxane having a viscosity η = 40 mPas were injected into the above circuit at 7 bar within 100 s from VA by means of P1 into M1 (nozzle diameters: 1.8/0.9 mm). After the addition was completed, the pre-emulsion was pumped into the buffer vessel VD and homogenised at a slightly later stage by means of P4 in one pass in jet disperser STR-D with a pressure drop of ΔP = 250 bar. The results are given in Table 5.

Table 5

Example no.	Pass no.	Particle size Ø [µm]	Time [min/s]	Total emulsification time [min/s]	Stability [months]
16	V		2'10"		
	1	0.368	4'40"		>6
				6'50"	

D. Silicone emulsion in the mixing station

Example 17

A mixture of 96.6 g of an ethoxylated tridecylalcohol with an HLB value of 11.4, 552.72 g of a polydimethylsiloxane with a viscosity η = 500 mPas, 994.84 g of a mineral oil raffinate with a boiling range of 382 - 432°C and 691.04 g of a di- (2-ethylhexyl) phthalate was pumped out of the vessel VA at a pressure of 3 bar first for one minute via M1 (nozzle diameters: 1.4/0.6 mm) in the circuit

VA→P1→M1→VA. A solution of 464.52 g of water and 0.28 g of benzylalcohol monohemiformal was then injected into this circuit within 3 minutes at a pressure of 3.5 - 4 bar via VC→P3→M1. After all the water had been added, pumping was continued in the circuit VA→P1→M1→VA for another 3 minutes at a pressure of 3 bar. This circuit was maintained for another 10 minutes with a pressure of 12 bar. A high-viscosity stable emulsion is obtained. The results are given in Table 6.

Table 6

Example no.	Time [min/sec]	Particle size Ø [μm]	Viscosity [mPas]	Stability [months]
17	17	1.748	2670	>6

Example 18 (according to the invention)

2800 g of a polydimethylsiloxane with a viscosity $\eta = 1000$ mPas were injected via the active substance circuit VA→P1→M1→VA into a solution of 171.9 g of an ethoxylated triglyceride with an HLB value of 18.1 and 148.1 g of an ethoxylated tridecyl alcohol with an HLB value of 11.4 in 800 g of water which was situated in the circuit VC→P3→M1. The initial absolute pressure of the active substance circuit was raised in so doing from 5 to 12 bar within 9 minutes. The pressure of the circuit VC→P3→M1 accompanied this increase - 2 bars lower in each case. After a total of 12 minutes, the feed of active substance had ended and a viscous white paste was obtained. This is pumped, with cooling, for another 14 minutes in the circuit VC→P3→M1 at 10 bar.

4080 g of water were then injected at 25°C from VB by means of P2 at a pressure of 12 bar in approx. 5 minutes. In so doing, the pressure fell to 4.5 bar as the dilution increased in the circuit VC→P3→M1, the pump P2 accompanying this fall at a pressure 2 bars higher. After all the water had been added, the pressure in the circuit

VC→P3→M1 was raised to 80 bar and the emulsion was removed from the mixing station via M1.

A low-viscosity, stable emulsion was obtained.

The results are given in Table 7.

__Example 19__ (according to the invention)

2800 g of a polydimethylsiloxane with a viscosity η = 350 mPas were injected via the active substance circuit VA→P1→M1→VA into a solution of 171.9 g of an ethoxylated triglyceride with an HLB value of 18.1 and 148.1 g of an ethoxylated tridecylalcohol with an HLB value of 11.4 in 800 g of water which was situated in the circuit VC→P3→M1. The initial absolute pressure of the active substance circuit was raised in so doing from 7 to 10 bar within 6 minutes. The pressure of the circuit VC→P3→M1 accompanied this increase - 2 bars lower in each case. After a total of 6 minutes, the feed of active substance had ended and a viscous white paste was obtained. This was pumped, with cooling, for another 20 minutes in the circuit VC→P3→M1 at 10 bar.

4080 g of water were then injected at 25°C from VB by means of P2 at a pressure of 10 bar within approx. 5 minutes. In so doing, the pressure fell to 4 bar as the dilution increased in the circuit VC→P3→M1, the pump P2 accompanying this fall at a pressure 2 bars higher. After all the water had been added, the pressure in the circuit VC→P3→M1 was raised to 80 bar and the emulsion was removed from the mixing station via M1.

A low-viscosity, stable emulsion was obtained.

The results are given in Table 7.

Table 7

Example no.	Time [min/sec]	Particle size Ø [µm]	U_{90}	Stability [months]
18	32	0.689	1.541	>6
19	32	0.531	1.168	>6

PCT/EP98/06058

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L99191PCT

CLAIMS (December 7, 1999)

1. A device for the preparation of a silicon- and/or silane emulsion of a silicone-containing and/or silane-containing active substance component and an aqueous phase, with a first mixing station for the emulsion components fed by means of pumps (P1, P2, P3) from storage tanks (VA, VB, VC) characterised in that

- the first mixing station has a mixing apparatus (M1), in which nozzles (2,4) mix a jet of active substance with the aqueous phase (3) to a pre-emulsion (5),
-
- the distance between the nozzles (2,4) is 1 to 10 times, preferably 2 to 4 times the diameter of the second nozzle (4),
-
- the diameter of the second downstream nozzle (4) is about 2 to 3 times as large as the diameter of the first nozzle,
- the mixing station is connected to a jet disperser (STR-D) (6), whereby the jet disperser (6) receives the pre-emulsion (5) leaving the mixing station,
- the pressure drop in the jet disperser (6) is between 2 and 1000 bar, preferably between 5 and 600 bar,
- and in that an intermediate container (VD) acting as a buffer vessel is connected to the mixing apparatus (M1), and that the jet disperser (6) receives the pre-emulsion (5) via the intermediate container (VD).

2. A device according to claim 1, characterised in that the mixing station has a pre-homogenisation apparatus (VC, P3), in which the pre-emulsion is pre-homogenised in a circuit.

3. A device according to one of claims 1 to 2, characterised in that a dilution apparatus (VB, P2) is arranged before the mixing station and the jet disperser (6).

4. A device according to one of claims 1 to 3, characterised in that the mixing apparatus (M1) is composed of two nozzles (2,4) arranged behind the other.

5. A device according to claim 4, characterised in that the pressure difference between the nozzles (2,4) of the mixing apparatus (M1) is between 1 to 10 bar, preferably between about 2 to 3 bar.

6. A device according to one of claims 1 to 5, characterised in that the first nozzle (2) of the mixing apparatus (M1) injects the jet of active substance (1) into the aqueous phase (3) fed in, and in that the second nozzle (4) intensively mixes and homogenises the jet of active substance (1) with the aqueous phase (3).

7. A device according to one of claims 1 to 6, characterised in that the jet disperser (6) is composed of several nozzles (10,12) arranged one behind the other.

8. A device according to one of claims 1 to 7, characterised in that the absolute pressure drop in the mixing station is between 2 and 100 bar, particularly between 2 and 60 bar.

9. A device according to claims 3 to 8, characterised in that the dilution apparatus is composed of a container (VB) containing residual water and optional additives and a pump (P2) by means of which water may be added to the pre-emulsion by means of the nozzle (2) of the mixing unit (M1)

10. A device according to one of claims 1 to 9, characterised in that the jet disperser (6) is connected to a storage tank (VE), from which the emulsion can be fed again to the jet disperser (6) by means of a pump (P5).

11. A process for the preparation of fine-particle aqueous silicone and/or silane-emulsions with a U_{90} value of less than 1.2 using the device according to claim 1, comprising

- the preparation of a pre-emulsion by injecting the silicone and/or silane component into an aqueous phase containing emulsifier in a mixing station, whereby a pressure difference depending on the nozzle dimensions of a maximum of 10 bar is maintained between the two streams with an absolute pressure drop of less than 100 bar,

- the homogenisation of the pre-emulsion is accomplished by means of a jet disperser (6), whereby the U_{90} value is determined according to the following formula:

$$U_{90} = \frac{d90 - d10}{d50}$$

in which d10 and d90 represent the diameter of the smallest (d10) and the largest (d90) particles remaining after subtraction of 10% by weight of the particles with the smallest (d10) and the largest (d90) diameters from a given quantity of particles, and in which the d50-value represent the diameter of the particle, that is larger as 50% by weight of all the particles and smaller than 50% by weight of all the particles.

12. A process according to claim 11, characterised in that the homogenisation takes place in a jet disperser, which has a maximum pressure drop of up to 1000 bar.

13. A process according to claim 12, characterised in that the pre-emulsion leaving the mixing station is fed directly or via a buffer vessel to the jet disperser.

14. A process according to claim 12, characterised in that the pre-emulsion is pre-homogenised in the mixing station in a circuit before being fed to the jet disperser.

15. A process according to claim 13, characterised in that the pre-emulsion is homogenised with a deficient amount of water in the mixing station in a circuit before being fed to the jet disperser where it is optionally inverted and then brought to the required concentration by dilution.

16. A process according to claim 13, characterised in that pre-emulsion is homogenised with a deficient amount of water in the mixing station in a circuit, and then brought to the required concentration with water by means of a downstream dilution apparatus before being fed to the jet disperser.

17. A process according to claims 14 and 15, characterised in that the dilution water contains thickeners.

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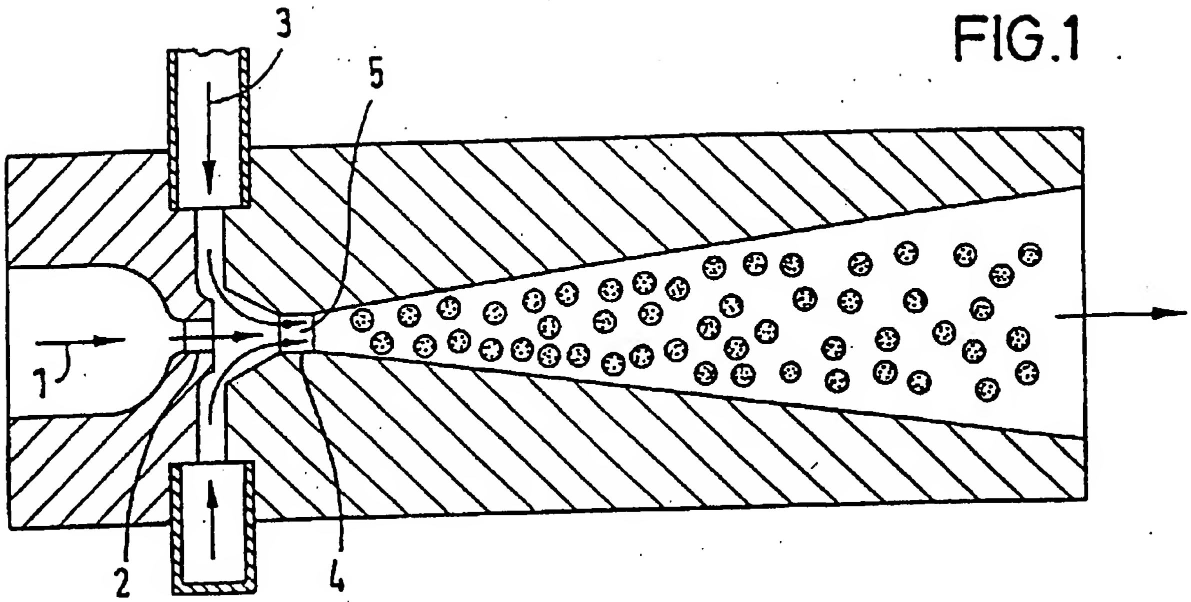


FIG.1

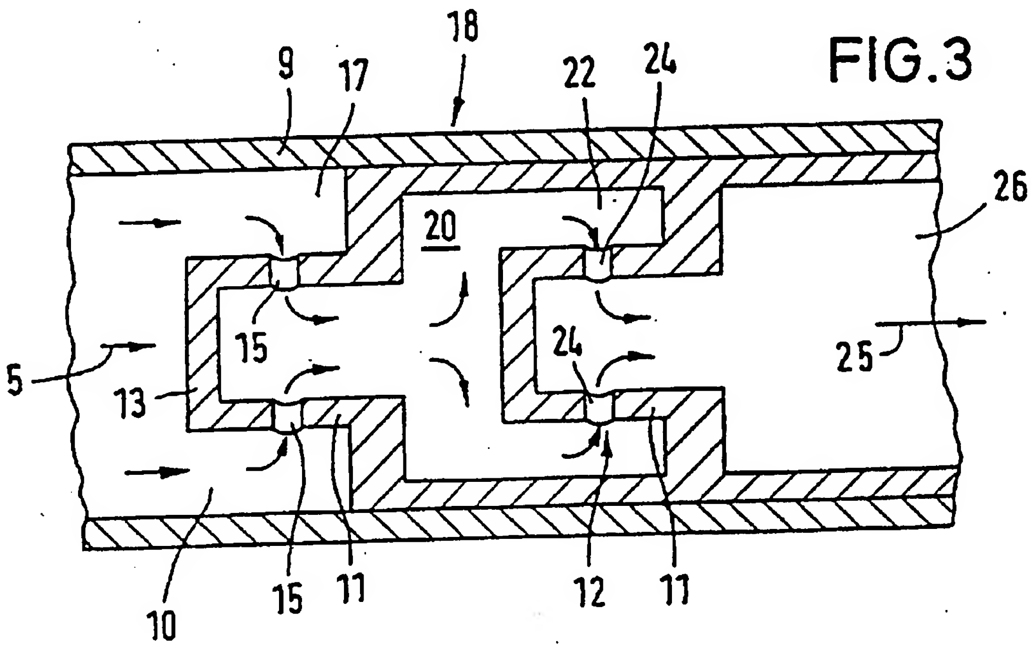


FIG.3

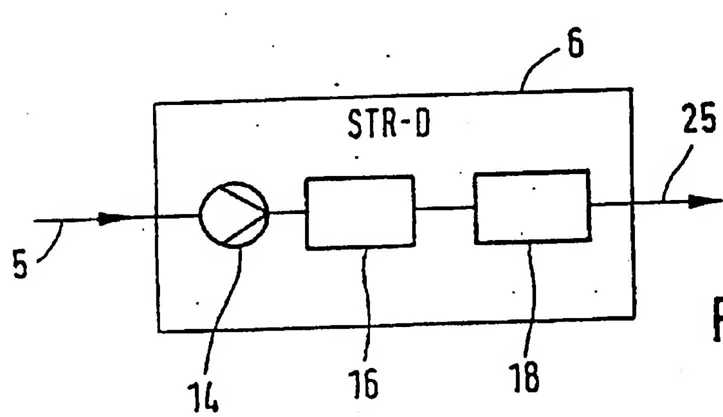


FIG.4

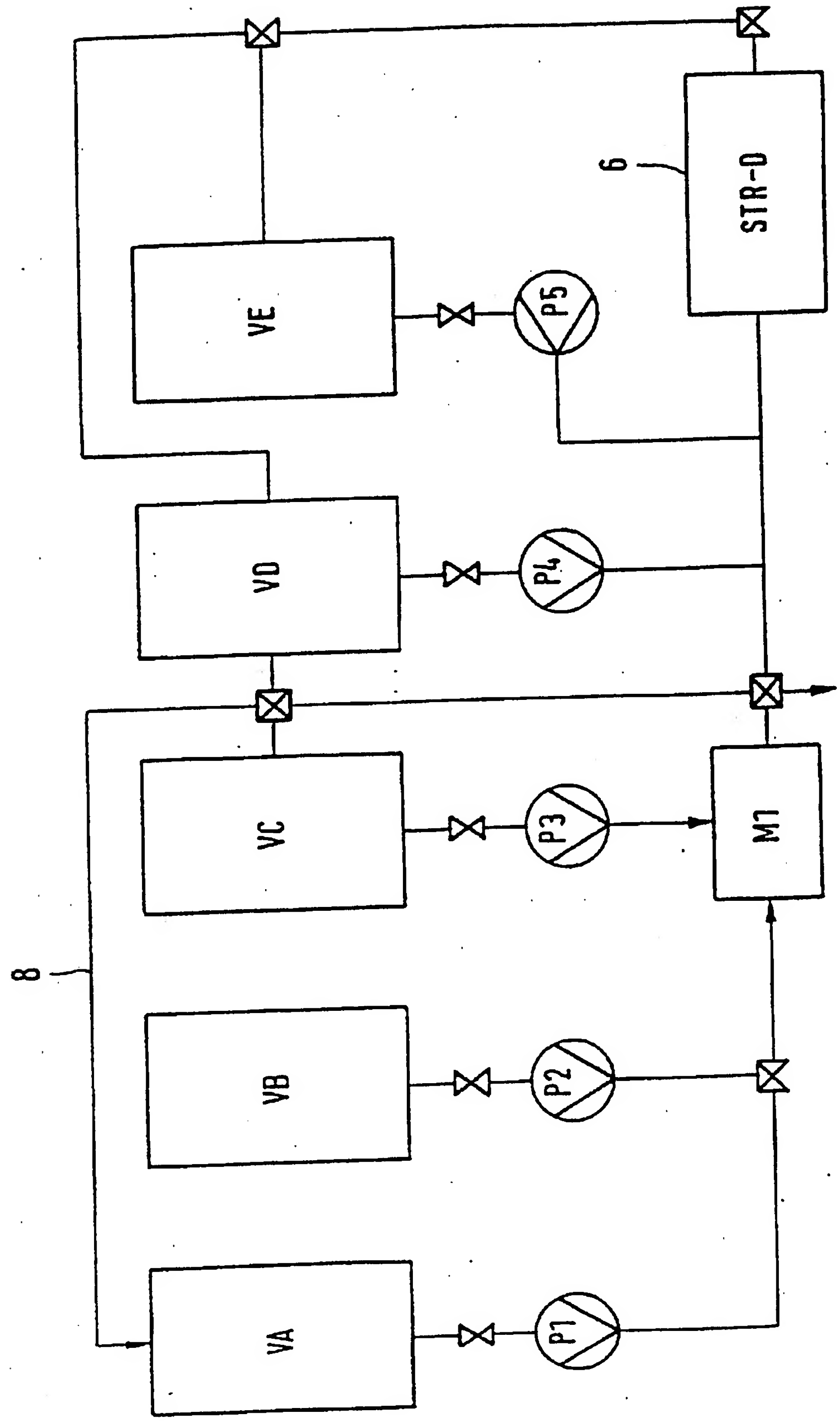


FIG.2

FIG.5

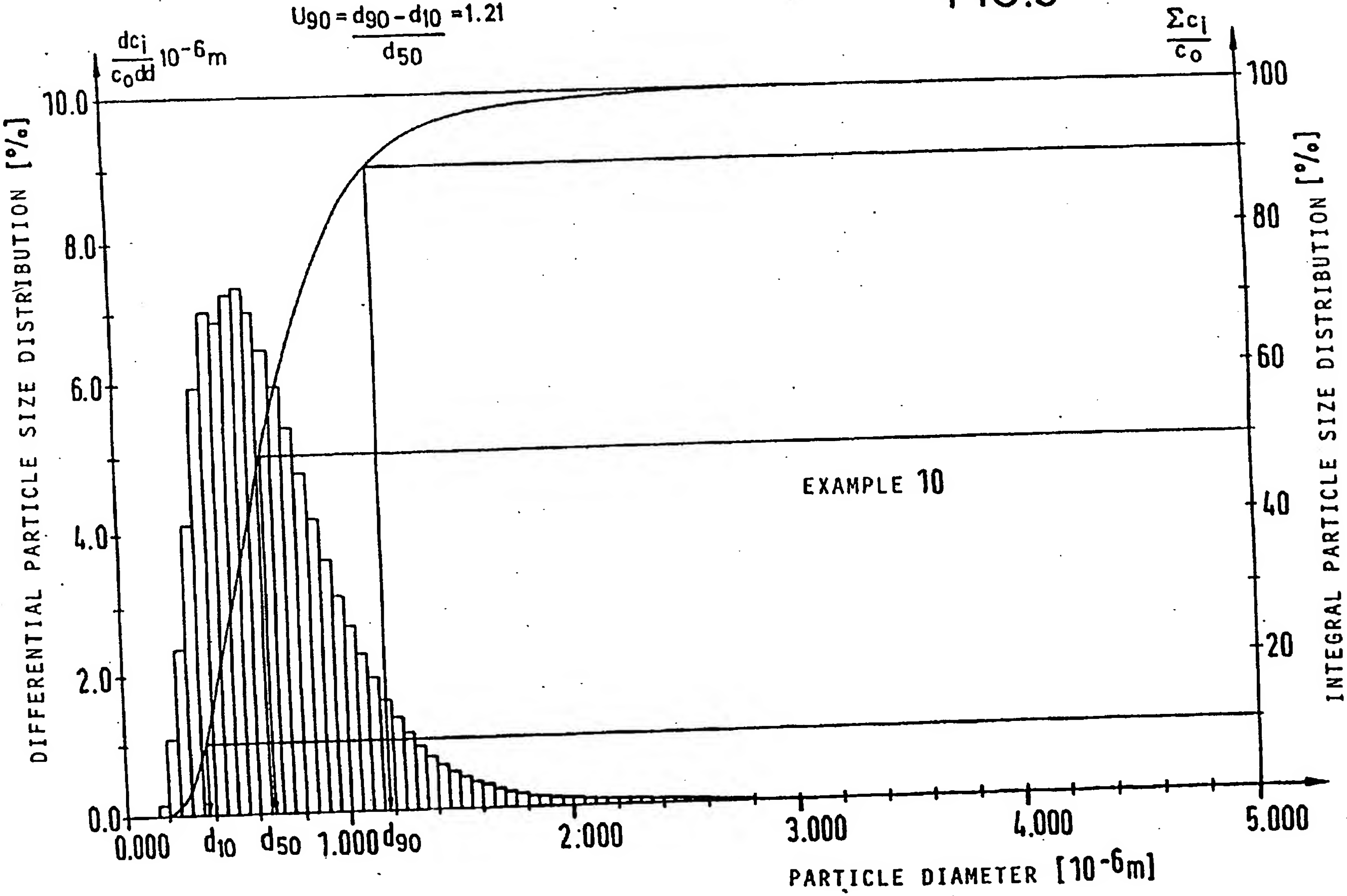
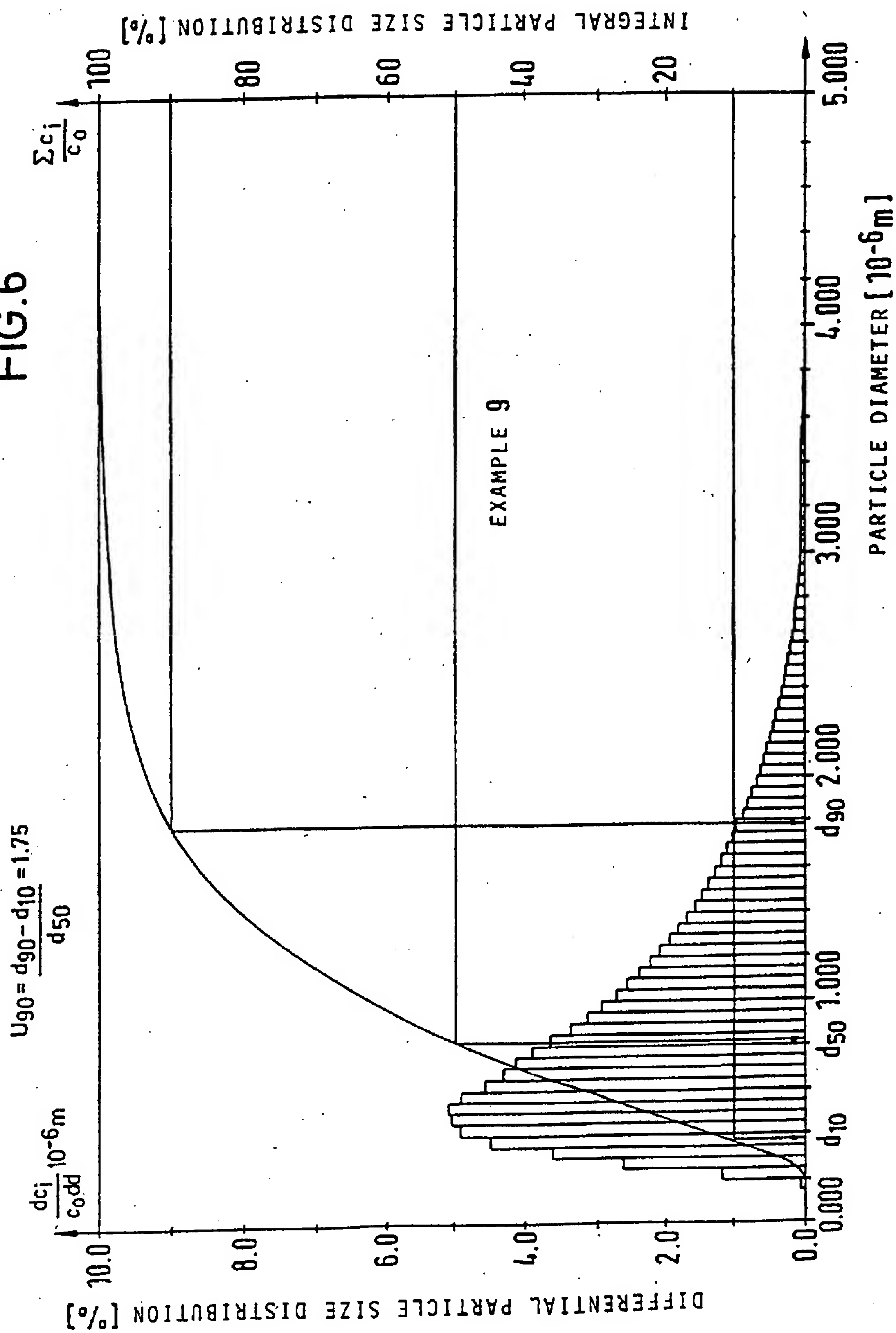

$U_{90} = \frac{d_{90} - d_{10}}{d_{50}} = 1.21$
$\frac{dc_i}{c_o dd} 10^{-6}m$
$\frac{\Sigma c_i}{c_o}$
10.0
8.0
6.0
4.0
2.0
0.0
100
80
60
40
20
DIFFERENTIAL PARTICLE SIZE DISTRIBUTION [%]
INTEGRAL PARTICLE SIZE DISTRIBUTION [%]
EXAMPLE 10
0.000
d_{10}
d_{50}
1.000
d_{90}
2.000
3.000
4.000
5.000
PARTICLE DIAMETER [10^{-6}m]

FIG.6


INTEGRAL PARTICLE SIZE DISTRIBUTION [%]
100
80
60
40
20
$\frac{\Sigma c_i}{c_o}$
EXAMPLE 9
$U_{90} = \frac{d_{90} - d_{10}}{d_{50}} = 1.75$
$\frac{dc_i}{c_o dd} 10^{-6}m$
10.0
8.0
6.0
4.0
2.0
0.0
DIFFERENTIAL PARTICLE SIZE DISTRIBUTION [%]
0.000
d_{10}
d_{50}
1.000
d_{90}
2.000
3.000
4.000
5.000
PARTICLE DIAMETER [10^{-6}m]

DIFFERENTIAL AND INTEGRAL PARTICLE SIZE DISTRIBUTION

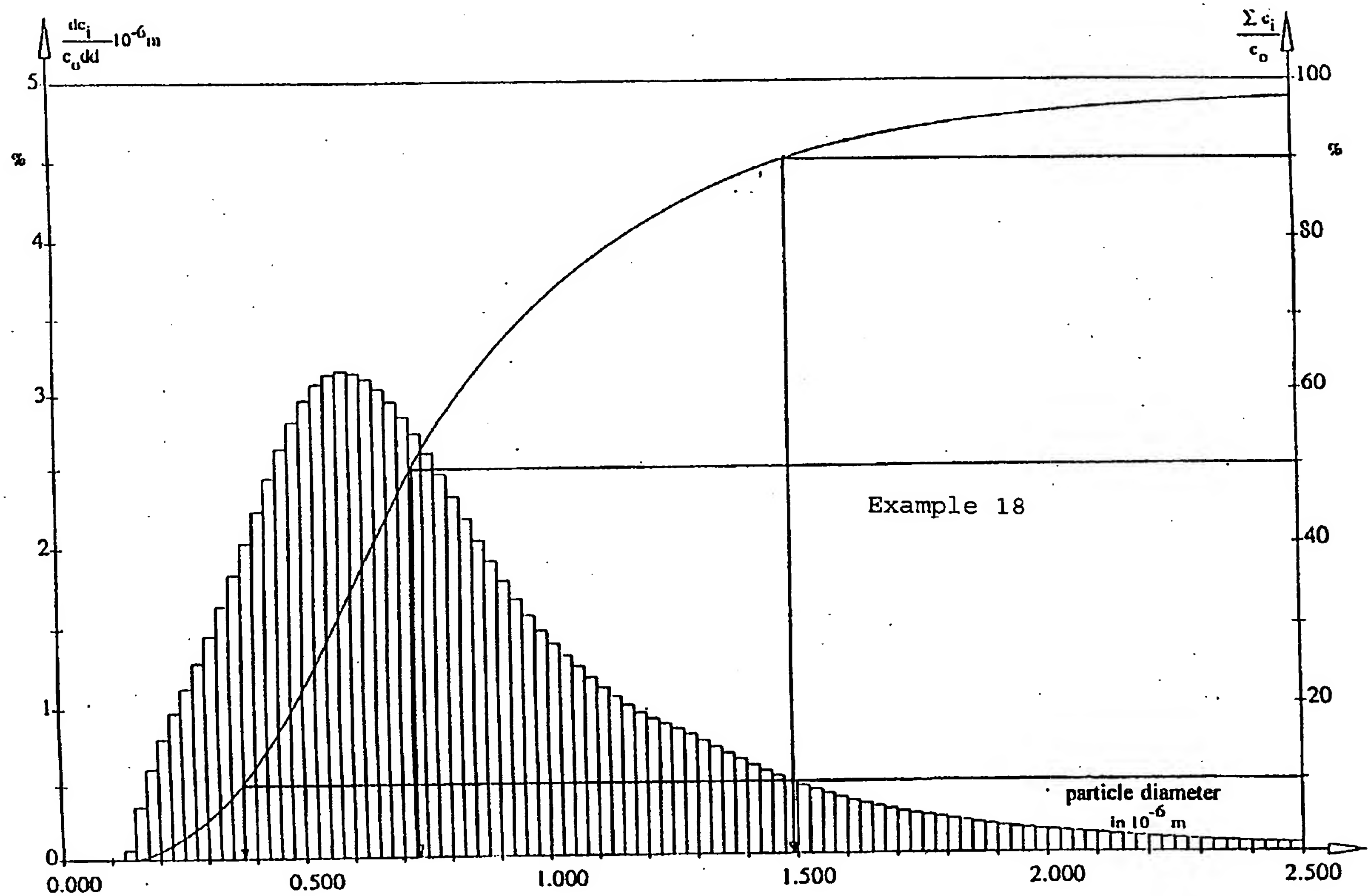


FIG. 7

FIG. 8

DIFFERENTIAL AND INTEGRAL PARTICLE SIZE DISTRIBUTION